A and the ionicity of the lattice at the impurity site. As far as the g values and the a values are concerned, quantitative estimates of the effects of covalency require an accurate knowledge of the environment of the ion.

ACKNOWLEDGMENTS

I wish to acknowledge the interest of Dr. R. W.Keyes in this research. I also would like to thank Dr. F. Jona for growing the crystals and E. Tynan for aid in taking the paramagnetic data.

PHYSICAL REVIEW VOLUME 131, NUMBER 2 15 JULY 1963

Junction Potential Studies in Tunnel Diodes

W. BERNARD, H. ROTH, A. P. SCHMID, AND P. ZELDES
Raytheon Research Division, Waltham, Massachusetts
(Received 18 February 1963)

A unique model is proposed for the potential distribution in the junction region of a tunnel diode. The essential feature of this model, in addition to band tailing, is a discontinuity in the band edges at the n-p interface arising from a difference in the electron affinities of degenerate n- and p-type semiconductors. In connection with the proposed description of a tunnel diode junction, precise capacitance measurements have been carried out on a series of germanium units at 78°K. The experimentally determined values of the capacitance built-in voltage are in substantial agreement with the theoretical prediction, $eV_b=E_{g0}+\frac{1}{3}(\xi_n+\xi_p)$, and thus lend strong support to the validity of the discontinuity model. The temperature dependence of the built-in voltage is also discussed.

MANY fundamental properties of the tunnel diode can be reasonably well explained on the basis of a degenerate semiconductor model in which the intrinsic energy band structure is retained, the appropriate conducting band simply being filled to degeneracy by the addition of a large concentration of suitable impurity atoms. Using this band picture it is possible, for example, to account for the essential behavior of the current-voltage characteristic, including the negative resistance,[1,2] the existence of phonon-assisted processes,[3,4] and the pressure[5] and magnetic field[6] dependences. Further, by introducing into the forbidden band gap energy levels appropriate to deep-lying impurities[7] and lattice defects[8] one can account in large measure for the excess current observed at increased forward bias.

However, it seems clear that further progress in understanding the various properties exhibited by tunnel diodes requires the adoption of a more realistic description of degenerate semiconductors. Pankove's optical studies, both on bulk germanium[9] and germanium tunnel diode junctions,[10] first suggested the inadequacy of the conventional energy-band description. More recently, Sommers[11] and Meyerhofer and his coworkers[12] have made a systematic study of the electrical properties of germanium junctions and interpreted a large variety of data in terms of existing theories. They cannot, however, account for the built-in potential determined from junction capacitance measurements. Whereas the conventional junction model predicts a capacitance built-in potential considerably in excess of the band gap, previous experimental results, obtained at room temperature, have yielded values consistently lower than the band gap.

The correct interpretation of the degenerate band structure must lead to a clarification of the junction-capacitance anomaly. In this note we propose a unique model of the potential distribution in the junction region of a tunnel diode. The essential feature of this model, which is based on fundamental considerations, is a discontinuity in the band edges at the n-p interface of the junction. The results of a series of precise junction capacitance measurements performed at 78°K are presented and compared with predictions based on the discontinuity model. The temperature dependence of the capacitance built-in voltage is also discussed.

The modifications which occur in the energy band spectrum of a semiconductor when extremely high concentrations of simple donor or acceptor impurities are added can be visualized in the following way. At low impurity concentrations, each additional impurity merely removes a conducting state from the edge of the conduction (or valence) band and replaces it with a set of

[1] L. Esaki, Phys. Rev. **109**, 603 (1959).
[2] E. O. Kane, J. Appl. Phys. **32**, 83 (1961).
[3] L. V. Keldysh, Zh. Eksperim. i Teor. Fiz. **34**, 962 (1958) [translation: Soviet Phys.—JETP **7**, 665 (1958)].
[4] N. Holanyak, I. A. Lesk, R. N. Hall, J. J. Tiemann, and H. Ehrenreich, Phys. Rev. Letters **3**, 167 (1959).
[5] S. L. Miller, M. I. Nathan, and A. C. Smith, Phys. Rev. Letters **4**, 60 (1960).
[6] A. R. Calawa, R. H. Rediker, B. Lax, and A. L. McWhorter, Phys. Rev. Letters **5**, 55 (1960).
[7] C. T. Sah, Phys. Rev. **123**, 1594 (1961).
[8] A. G. Chynoweth, W. L. Feldman, and R. A. Logan, Phys. Rev. **121**, 684 (1961); R. S. Claassen, J. Appl. Phys. **32**, 2372 (1961).
[9] J. I. Pankove, Phys. Rev. Letters **4**, 454 (1960).
[10] J. I. Pankove, Phys. Rev. Letters **4**, 20 (1960).
[11] H. S. Sommers, Jr., Phys. Rev. **124**, 1101 (1961).
[12] D. Meyerhofer, G. A. Brown, and H. S. Sommers, Jr., Phys. Rev. **126**, 1329 (1962).

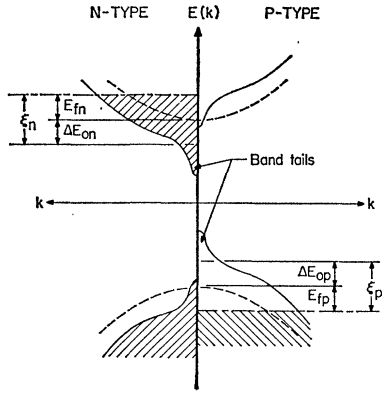

FIG. 1. Band structure of degenerate n- and p-type semiconductors. Dashed lines show energy spectrum for intrinsic material.

bound, hydrogenic-like states in the forbidden energy gap,[13] leaving the conduction band essentially unmodified. As intermediate concentrations of impurities are added, spatial overlap of the impurity orbitals can give rise to the formation of impurity bands,[14] with still negligible effect on the parent conduction band. However, as even higher impurity concentrations are attained ($\sim 10^{18}/\text{cm}^3$ for germanium), screening of the impurity potentials by the free electrons becomes so effective that bound impurity states can no longer exist. The impurity ions must now be regarded as an integral part of the host crystal and their contribution to the crystalline potential included in any calculation of the energy band structure.

Parmenter[15] has derived the energy spectrum of a crystal containing a degenerate concentration of randomly spaced impurities using infinite-order perturbation theory in which only those terms linear in the impurity concentration are retained. The essential features of Parmenter's results, when applied to the case of a simple degenerate semiconductor, are indicated in Fig. 1. As the Fermi level in the conduction band is raised an energy E_{fn} above the intrinsic band edge by the addition of donor impurities, both conduction and valence bands are depressed an energy ΔE_{0n} by the attractive potential of the ionized donors. In addition, the random spatial distribution of the impurities throughout the crystal lattice gives rise to tailing of the energy spectrum near the band edges. Only a small fraction of the conduction electrons present are found in the band tail because of the low density of states associated with this region of the spectrum. A similar situation occurs in the case of p-type material, except that the bands are raised by the repulsive potential of the ionized acceptors.

The energy ΔE_{0n} through which the degenerate band edge is moved represents a change in the electron affinity of the semiconductor, and, according to Parmenter,[15] is determined by the electronic screening radius, or Debye length, λ as

$$\Delta E_{0n}=4\pi e^2 n\lambda^2/\kappa, \tag{1}$$

where n is the free-electron (impurity) concentration, e the electronic charge, and κ the dielectric constant. Equation (1), which is valid when the electronic screening precludes the formation of bound impurity states, can be deduced in a straightforward manner by considering the interaction between the impurity atoms and the intrinsic conducting band wave function. Each impurity potential V moves a band state k through an energy given by the diagonal matrix element $\langle k|V|k\rangle$. Thus, for a system of n impurities, the total energy displacement of the state k is

$$\Delta E_k=n\langle k|V|k\rangle. \tag{2}$$

Although various techniques have been employed in the solution of the degenerate band structure problem, the energy displacement ΔE_k of Eq. (2) has been a common feature of the results.[15–17] If the screened impurity potential $V=-(e^2/\kappa r)e^{-r/\lambda}$ is used, then Eq. (2), in the effective mass approximation, yields Eq. (1). We further note that Conwell and her co-workers[17] have undertaken a critical evaluation of the Parmenter treatment and conclude that it is rigorously valid though second order in V.

In addition to the foregoing one-electron treatment, it is also of interest to note that Wolff[18] has recently undertaken an investigation of the band structure of degenerate semiconductors in the high-density limit using many-body perturbation theory. He finds a similar displacement of the energy bands, which, however, arises from the electron exchange interaction rather than from the attractive potentials of the screened impurity ions. The high-density criterion appears to be satisfied in germanium only for impurity concentrations greater than $\sim 10^{20}$ cm^{-3}, which is somewhat in excess of the doping levels present in the diodes we have studied. Over the range of impurity concentrations of interest here the magnitude of the energy band displacement obtained by Wolff seems to be in at least qualitative agreement with that derived in the present paper on the basis of the Parmenter result.

The screening radius λ can be expressed in terms of the ratio of the diffusion constant D to the mobility μ as

$$\lambda^2=\frac{\kappa}{4\pi en}\frac{D}{\mu}, \tag{3}$$

[13] J. C. Slater, Phys. Rev. **76**, 1592 (1949); J. M. Luttinger and W. Kohn, *ibid.* **97**, 869 (1955).
[14] W. Baltensperger, Phil. Mag. **44**, 1355 (1953).
[15] R. H. Parmenter, Phys. Rev. **104**, 22 (1956).
[16] M. Lax and J. C. Phillips, Phys. Rev. **110**, 41 (1958).
[17] E. M. Conwell and H. Schlosser, Bull. Am. Phys. Soc. **7**, 214 (1962); E. M. Conwell and B. W. Levinger, in *Proceedings of the 1962 International Conference on the Physics of Semiconductors, Exeter*, edited by A. C. Stickland (The Institute of Physics and The Physical Society, London, 1962), p. 227.
[18] P. A. Wolff, Phys. Rev. **126**, 405 (1962); in *Proceedings of the 1962 International Conference on the Physics of Semiconductors Exeter*, edited by A. C. Stickland (The Institute of Physics an The Physical Society, London, 1962), p. 220.

so that Eq. (1) becomes

$$\Delta E_{0n}=eD/\mu. \tag{4}$$

The mobility-diffusion ratio is, in turn, determined by the Einstein relation, the general form of which, according to Kubo,[19] is

$$\frac{\mu}{eD}=\frac{1}{n}\frac{dn}{dE_{fn}}. \tag{5}$$

In Eq. (5) *E_{fn} is the absolute Fermi level*, that is, the Fermi level referred to some fixed energy zero. In the case of a degenerate semiconductor the band edge cannot be taken as the reference energy, since its position, in contrast to the nondegenerate case, is a function of the free electron concentration. From Eqs. (4) and (5), letting $n\propto(E_{fn}+\Delta E_{0n})^{3/2}$ and taking into account the simultaneous motion of the band edge and the Fermi level, we find that the shift in the band edge for a degenerate semiconductor at $T=0°\mathrm{K}$ is determined by the equation

$$\Delta E_{0n}=\frac{2(E_{fn}+\Delta E_{0n})}{3[1+d(\Delta E_{0n})/dE_{fn}]}. \tag{6}$$

The solution of Eq. (6) is

$$\xi_n\left(1-\frac{5\Delta E_{0n}}{2\xi_n}\right)^{2/5}=\text{const}, \tag{7}$$

where $\xi_n=(E_{fn}+\Delta E_{0n})$ is the energy penetration of the Fermi level into the degenerate band. With the boundary condition[20] that $\Delta E_{0n}/\xi_n$ remains finite in the limit $\xi_n\to 0$, Eq. (7) yields the result

$$\Delta E_{0n}=\tfrac{2}{5}\xi_n,\quad E_{fn}=\tfrac{3}{5}\xi_n. \tag{8}$$

A similar result is obtained for degenerate p-type material.

It follows from the above considerations that a step junction constructed from uniformly doped degenerate materials will exhibit at the n-p interface the band-edge discontinuity

$$\Delta=\tfrac{2}{5}(\xi_n+\xi_p) \tag{9}$$

shown in the potential diagram of Fig. 2. Of course, this picture may represent an idealization of the actual situation in certain cases. In the transition region of the junction the screening of the impurity potentials is effected by the mobile carriers in the bulk material on either side. Since the energy spectrum is a function of the electronic screening, the details of the band structure in the transition region will be modified in a complex manner according to the width of the junction and the impurity concentrations in the n- and p-type materials.

[19] R. Kubo, J. Phys. Soc. Japan **12**, 570 (1957).

[20] Letting $\xi_n\to 0$ in Eq. (7) may not be rigorously valid, since in this limit the material is no longer degenerate. However, the error involved should in any case be small for reasonably high doping levels.

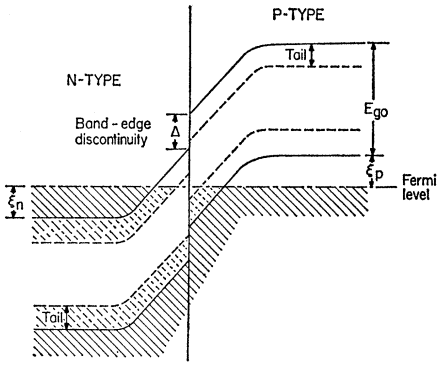

FIG. 2. Proposed discontinuity model of degenerate p-n junction.

Because tunnel diode junctions are characteristically extremely narrow, however, the extent of such modification is expected to be slight. In any event, the essential feature of the model remains: The difference between the electron affinities of bulk n- and p-type degenerate semiconductors gives rise to an effective discontinuity in the band edge at the n-p interface as given by Eq. (9).

Although the proposed model may have implications with respect to several tunnel diode properties, the junction capacitance should be particularly sensitive to the existence of the band-edge discontinuity. Assuming the band structure in the transition region on either side of the n-p interface to be that established for the respective bulk materials, the solution to Poisson's equation for the proposed model, neglecting the band tailing, yields a junction capacitance in the familiar form

$$C=C_0(1-V/V_b)^{-1/2}, \tag{10}$$

with the important exception that here the built-in voltage V_b is given by

$$eV_b=E_{g0}+\tfrac{1}{5}(\xi_n+\xi_p). \tag{11}$$

E_{g0} is the intrinsic band gap of the material. The zero-bias capacitance C_0 is given by the expression

$$C_0=\left[\frac{N_aN_d e\kappa A^2}{8\pi V_b(N_a+N_d)}\right]^{1/2}. \tag{12}$$

In Eq. (12), N_d and N_a are the (compensated) donor and acceptor concentrations in the n- and p-type materials, respectively, and A is the junction area.

We have performed capacitance measurements[21] on a number of forward-biased germanium tunnel diodes at 78°K. A series of diodes was fabricated with In-Ga-Zn dots alloyed on base material doped with from 1.5×10^{19} to 3.0×10^{19} arsenic impurities cm^{-3}. The diodes were mounted in modified microwave packages to minimize inductive effects, and the measurements were carried out at 15 and 30 Mc/sec using an impedance bridge.

[21] W. Bernard, H. Roth, A. P. Schmid, and P. Zeldes, Bull. Am. Phys. Soc. **7**, 232 (1962).

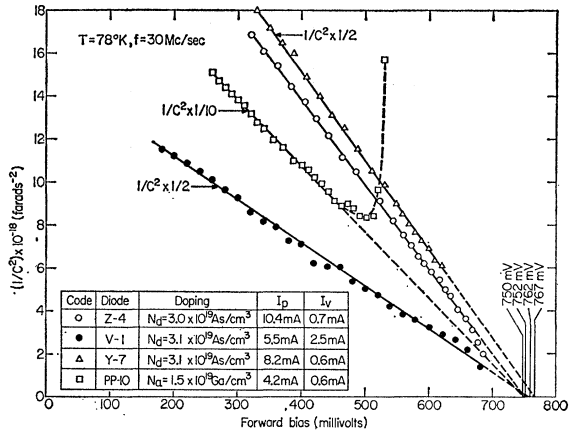

FIG. 3. $1/C^2$ versus forward bias voltage for several germanium tunnel diodes. Capacitance built-in voltages are indicated. The large anomalous "inductive" behavior of the p-base unit at high forward bias cannot be accounted for by the package and circuit inductance.

The sensitivity of the detection circuitry was such that ac signals of only 1 mV across the diode were required. Typical experimental results are presented in Fig. 3, which shows $1/C^2$ as a function of forward bias for several units. The capacitance data in all cases exhibit the square-root voltage dependence characteristic of uniformly doped step junctions. At 78°K the extrapolated capacitance built-in voltages are consistently found to be somewhat greater than the intrinsic band gap, which at this temperature is 0.73 eV, in agreement with the prediction of the discontinuity model of the junction potential.

Also shown in Fig. 3 are capacitance data typical of those obtained for diodes fabricated with Sn-As dots alloyed on base material doped with $\sim 1.5\times 10^{19}$ gallium impurities cm^{-3}. On none of the several p-base diodes studied was it possible to obtain significant experimental results over a bias range greater than 200 mV, since at high forward bias the measured capacitance decreased with increasing bias far more rapidly than could be accounted for by package inductance. Although the capacitance data for the p-base units were qualitatively consistent with those for the n-base units, we will not consider them here in further detail because of the uncertain origin of the anomalous "inductive" effect and the relatively large experimental scatter.

In order to obtain a detailed comparison between theory and experiment it is necessary to determine the Fermi energies ξ_n and ξ_p. The Fermi energy ξ_n was calculated from Hall measurements of the base material according to the four-ellipsoid conduction band model of germanium.[22] The calculation of the Fermi energy ξ_p requires a knowledge of the compensated concentration N_a of gallium in the recrystallized p-type region. Using the known concentration N_d of arsenic in the base material, together with the zero-bias capacitance per unit area C_0/A, N_a can be determined from the relation [see Eq. (12)]

$$N_a=\frac{N_d}{(e\kappa N_d/8\pi V_b)(A/C_0)^2-1}. \tag{13}$$

The value of C_0 is obtained by extrapolation of the $1/C^2$ versus V curve to zero bias. The junction area A, on the other hand, can be obtained accurately only by physical examination of the junction. A number of randomly selected diodes were multiply sectioned, etched, and microscopically examined to obtain accurate junction profiles. From the concentration N_a of gallium thus determined, the Fermi energy ξ_p was calculated according to the warped two-valence band model of Dresselhaus, Kip, and Kittel.[23,24]

Figure 4 shows the capacitance built-in voltage V_b as a function of the sum of the Fermi energies $(\xi_n+\xi_p)$ in the n- and p-type materials for those n-base diodes for which accurate area determinations have been made by metallographic sectioning. The estimated experimental error in the indicated values of V_b is ± 10 mV. The theoretical prediction of Eq. (11) based on the discontinuity model of the junction potential is also shown. We note that two of the experimental points deviate from the theoretical line by more than the experimental error. We are unable to account for the low built-in voltage exhibited by diode DD-8 on any reasonable basis. On the other hand, a possible explanation for the deviation of diode 4C-6 from the theoretical prediction will be discussed momentarily in connection with the temperature dependence of V_b.

Also included in Fig. 4 for comparison is the theoretical prediction based on the conventional model of

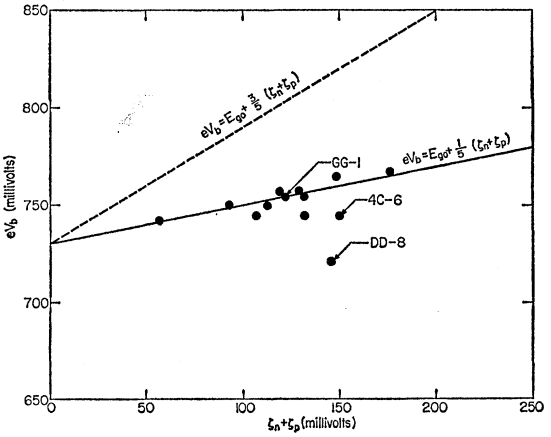

FIG. 4. Capacitance built-in voltage versus sum of Fermi level penetrations into the degenerate bands at 78°K. The solid line represents the theoretical prediction based on the discontinuity model, while the dashed line indicates the prediction of the conventional junction model.

[22] C. Herring, Bell System Tech. J. **34**, 237 (1955).

[23] C. Dresselhaus, A. F. Kip, and C. Kittel, Phys. Rev. **98**, 368 (1955).

[24] B. Lax and J. G. Mavroides, Phys. Rev. **100**, 1650 (1955).

the junction potential, which assumes that the only consequence of doping a semiconductor to degeneracy is the penetration of the Fermi level an energy ξ into the conducting band. In this case the band edges are continuous across the n-p interface, and the solution to Poisson's equation for a step junction at $T=0°K$ yields a capacitance-voltage relationship of the form of Eq. (10), where now

$$eV_b = E_{g0} + \tfrac{3}{5}(\xi_n + \xi_p). \tag{14}$$

It is apparent from Fig. 4 that the discontinuity model yields an adequate prediction of the experimental results, while the conventional junction model does not, thus lending strong support to the validity of the discontinuity model.

As has been mentioned, previously reported values for the capacitance built-in voltage in germanium tunnel diodes appear to differ markedly from the results presented here. Chynoweth and his co-workers,[25] Meyerhofer and his coworkers,[12] and Sommers[11] all report capacitance built-in voltages, measured at 300°K, consistently less than the intrinsic band gap. In order to investigate this apparent inconsistency, we have carried out capacitance measurements on several germanium diodes at various points in the temperature range 78 to 300°K. A typical result for the built-in voltage as a function of temperature is that shown in Fig. 5 for diode GG-1. Also shown for comparison is the intrinsic band gap of germanium. At 300°K, V_b is appreciably less than E_{g0}, in agreement with results quoted by other investigators.[11,12,25] As the temperature is reduced, V_b increases monotonically, becoming larger than E_{g0}. In the neighborhood of 78°K V_b appears to saturate, such that $d(eV_b)/dT$ approaches dE_{g0}/dT. It is precisely this low-temperature saturation effect that makes possible a valid prediction of V_b at 78°K based on the specific model considered in the present paper.

Figure 5 also shows eV_b versus T data for an atypical diode, 4C-6. It is seen that the crossover between the built-in voltage and the band gap occurs at a substantially lower temperature, and the data suggest that V_b has not yet saturated at $T=78°K$. We offer this as a possible explanation for the low value of V_b exhibited by diode 4C-6 in Fig. 4.

The dependence of the energy band discontinuity at the n-p interface on the screening of the impurity ions by the free carriers [see Eq. (1)] suggests that the temperature dependence of the capacitance built-in voltage may arise from a corresponding temperature dependence of λ^2. Independent evidence of the existence

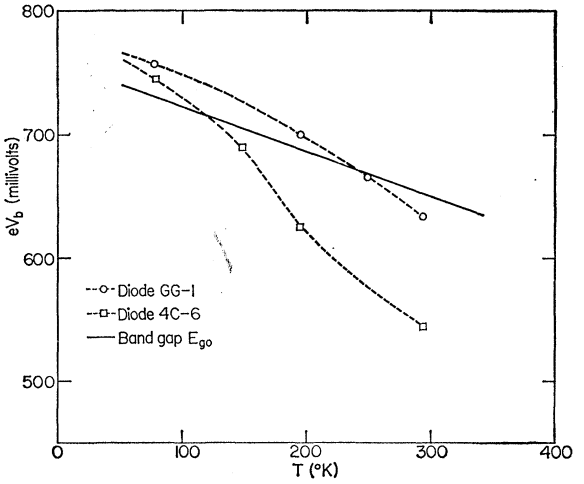

FIG. 5. Temperature dependence of the capacitance built-in voltage for two diodes studied. The solid line shows the temperature dependence of the intrinsic band gap.

of such a temperature dependence of the screening radius has been obtained in the course of galvanomagnetic studies on bulk samples of degenerate germanium.[26] The scattering relaxation time in these materials is found to be that appropriate to screened impurity scattering, and exhibits a saturation with temperature in the vicinity of 78°K similar to that exhibited by the capacitance built-in voltage of the diodes. Moreover, the relative magnitudes of the observed change with temperature of the capacitance built-in voltages of the diodes and the relaxation times in the bulk material are consistent with the assumption of a common temperature-dependent λ^2. Although, as the temperature is increased, one would expect the screening to become less effective due to enhanced thermal motion of the free carriers, no appreciable increase in λ^2 should occur so long as kT remains small compared to the Fermi energy. Thus, it appears that the proposed temperature dependence of λ^2 will have to be explained on the basis of other considerations, and as such remains an interesting problem for future investigation.

In addition to accounting for the observed junction capacitance behavior, the proposed discontinuity model should have further implications with respect to various tunneling, excess current, and recombination-radiation phenomena. We note, for example, that the potential discontinuity prevents spatial overlap of the degenerate n- and p-type regions at high forward bias, thereby limiting the contribution of direct generation-recombination processes to the total current.

[25] A. G. Chynoweth, W. L. Feldman, C. A. Lee, R. A. Logan, G. L. Pearson, and P. Aigrain, Phys. Rev. **118**, 425 (1960).

[26] W. Bernard, H. Roth, and W. D. Straub, Bull. Am. Phys. Soc. **8**, 224 (1963).